Rational design of hierarchically porous birnessite-type manganese dioxides nanosheets on different one-dimensional titania-based nanowires for high performance supercapacitors

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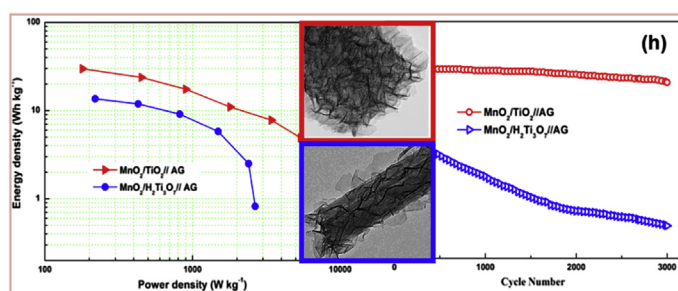[d] College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, PR China
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HIGHLIGHTS

- MnO_2 nanosheets were decorated on 1D TiO_2 nanowires by a facile and large-scale method.
- The MnO_2/TiO_2 core–shell architecture exhibited a high capacitance of 120 F g^{-1} (0.1 A g^{-1}).
- Excellent cycling stability: 93% capacitance retention after 3000 cycles.
- The asymmetric supercapacitor yielded a maximum energy density of 29.8 Wh kg^{-1}.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A facile and large-scale strategy of mesoporous birnessite-type manganese dioxide (MnO_2) nanosheets on one-dimension (1D) $H_2Ti_3O_7$ and anatase/TiO_2 (B) nanowires (NWs) is developed for high performance supercapacitors. The morphological characteristics of MnO_2 nanoflakes on $H_2Ti_3O_7$ and anatase/TiO_2 (B) NWs could be rationally designed with various characteristics (e.g., the sheet thickness, surface area). Interestingly, the MnO_2/TiO_2 NWs exhibit a more optimized electrochemical performance with specific capacitance of 120 F g^{-1} at current density of 0.1 A g^{-1} (based on MnO_2 + TiO_2) than $MnO_2/H_2Ti_3O_7$ NWs. An asymmetric supercapacitor of MnO_2/TiO_2//activated graphene (AG) yields a better energy density of 29.8 Wh kg^{-1} than $MnO_2/H_2Ti_3O_7$//AG asymmetric supercapacitor, while maintaining desirable cycling stability. Indeed, the pseudocapacitive difference is related to the substrates, unique structure and surface area. Especially, the anatase/TiO_2 (B) mixed-phase system can provide good electronic conductivity and high utilization of MnO_2 nanosheets.

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1. Introduction

Supercapacitors, owing to low cost, high power density, small size, rapid charging/discharging rates and long cycle life, are considered to be a kind of important energy conversion and storage

device [1–3]. According to charge storage mechanisms, super-capacitors can be classified into two types [4,5]: (I) Electrochemical double layer capacitors (EDLCs) are based on surface reaction at the electrode materials/electrolyte interface. Various carbon materials with high surface area such as carbon aerogels, grapheme and mesoporous carbons have been used as electrode materials or substrates for supercapacitors [6–8]. (II) Pseudocapacitors are based on Faradaic redox reactions occurring at the electrode materials surface. Transition-metal oxides (NiO, RuO_2, MnO_2, Co_3O_4, TiO_2 and ZnO) [9–13] and conducting polymers [14,15] generally display pseudocapacitive behavior. Potentially, the pseudocapacitors have much higher capacitance compared with the EDLCs [9–13].

Much effort has been devoted to improve the device energy and power densities of transition metal oxides owing to their easy availability as well as comparable electrochemical behavior [16], variable oxidation states and multi-electron transfer during the faradaic reactions [17]. In comparison to other transition metal oxides, manganese oxide-based supercapacitors are considered as alternative device for supercapacitors owing to their environmental friendliness, wide potential window, good electrochemical performance, natural abundance and low cost [18–20]. The charge storage mechanism for MnO_2 is widely accepted to be based on redox reactions, including (1) the surface adsorption of electrolyte cations; (2) the intercalation/de-intercalation of alkali cations in the bulk [6,21]. However, the densely packed structure, low surface area and poor electronic conductivity of MnO_2 severely limit practical capacitance [22–24]. Thus, various manganese oxide-based supercapacitors are developed to enhance electrical conductivity, morphological properties, porosity and surface area etc. [25] by introducing difference substrates, which can significantly affect electro activities and structural features of MnO_2 leading to high charge/discharge capacities and short diffusion paths for ion and electron transport which may improve the utilization of MnO_2 materials.

Among various substrates, one-dimensional (1D) inorganic nanostructured materials (nanowires and nanotubes arrays) have garnered sustained research interest owing to their promising charge transport ability, compared to traditional materials [26,27]. Among those 1D inorganic nanomaterials, titanic oxide-based nanowires seem to be extremely attractive for hybrid-supercapacitor applications because of their high chemical/thermal stability, suppression of structural distortion [28], enhanced cycling stability and improved reversibility [29,30], and more active sites for ions and electron to deliver a higher energy-density [31,32]. Moreover, the titanic oxide-based nanowires have higher electrical conductivity ($10^{-5} \sim 10^{-2}$ S cm^{-1}) than MnO_2 ($10^{-6} \sim 10^{-5}$ S cm^{-1}) [28]. In addition, it has been reported that, one-dimensional single-crystalline nanostructures are superior to polycrystalline counterparts in electron transport [33,34].

In this work, well-designed MnO_2-based nanostructured electrodes with two different 1D nanowires: (1) $H_2Ti_3O_7$ and (2) anatase/TiO_2 (B) are synthesized via an one-step hydrothermal method without carbon coating. The morphology, structure and electrochemical properties of the composites electrodes are examined. Moreover, the electrochemical properties of the asymmetric supercapacitors of MnO_2/TiO_2//AG and MnO_2//$H_2Ti_3O_7$//AG are investigated for comparison.

2. Experimental section

2.1. Synthesis of $H_2Ti_3O_7$ and TiO_2 NWs

All reagents were of analytical purity and used without any further purification. Synthesis of $H_2Ti_3O_7$ nanowires was performed via a hydrothermal process. In a typical synthesis, commercial anatase TiO_2 powders (0.4 g) were put into aqueous solution of 10 M NaOH (35 mL) in a Teflon-lined stainless steel autoclave (50 mL). The autoclave was kept at 180 °C for 48 h. After hydrothermal treatment, the resulting precipitates were acid-washed (0.1 M HCl solution) to realize the full-ion exchange from Na^+ to H^+. The final white products were then dried in vacuum at 80 °C for 8 h, and then calcined at 400 °C for 3 h in air to obtain the anatase/TiO_2 (B) nanowires.

2.2. Synthesis of the MnO_2 nanosheets on $H_2Ti_3O_7$ and TiO_2 NWs

In a typically synthesis, 25 mg $H_2Ti_3O_7$ (or TiO_2) were dispersed in $KMnO_4$ solution (40 mL, 0.01 M) by ultrasonication for 10 min. The mixed solution was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was directly put in an electric oven at 140 °C for 24 h and then cooled to room temperature. The black resultants were collected by centrifugation and dried at 60 °C for 12 h in a vacuum oven.

2.3. Materials characterization

The structure and morphology investigations of the samples were carried out with focused ion beam scanning electron microscopy (ZEISS AURIGA FIB/SEM) and transmission electron microscopy (TEM, ZEISS LIBRA 200). The chemical composition and crystallographic information of as-prepared products were established by powder X-ray diffraction (XRD, D/max 1200, Cu Kα). Nitrogen adsorption–desorption isotherms were obtained using a micromeritics ASAP 2020 sorptometer to assess surface area and porosity.

2.4. Electrochemical measurements

All the electrochemical tests were conducted with an electrochemical workstation (CHI 660E) using a conventional three electrode system where a mixture of active materials, carbon black, and polyvinylidene fluoride (PVDF) (7:2:1 wt.%), a Ag/AgCl and a platinum plate were used as working, reference electrodes and counter, respectively. The positive electrodes were investigated by cyclic voltammetry (CV) technique with varying the potential between 0 and 0.8 V at a rate ranged from 5 to 50 mV s^{-1}. Galvanostatic charge–discharge (GCD) experiments were performed with current densities of 0.1–10 A g^{-1} at a potential of 0–0.7 V. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range between 100 kHz and 0.01 Hz with a perturbation amplitude of 5 mV versus the open-circuit potential.

The electrochemical performance of asymmetric supercapacitor was measured with a two-electrode system including two slices of electrode material with the same size which were assembled together with filter paper soaked in 1 M Na_2SO_4 solution before being connected to the potentiostat. The MnO_2/TiO_2 or MnO_2/$H_2Ti_3O_7$ NWs were the positive electrode and activated graphenes (AG) were the negative electrode, respectively. CVs were recorded as scan rates of 5, 10, 20, 50, and 80 mV s^{-1}. GCD curves were obtained at constant current densities of 0.2, 0.5, 1, 2, 4 and 6 A g^{-1}. All the operating current densities were calculated based on the total weight of MnO_2/TiO_2 or $MnO_2/H_2Ti_3O_7$ NWs with AG.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns of $H_2Ti_3O_7$ NWs and MnO_2/$H_2Ti_3O_7$ NWs. Almost all the identified peaks can be perfectly
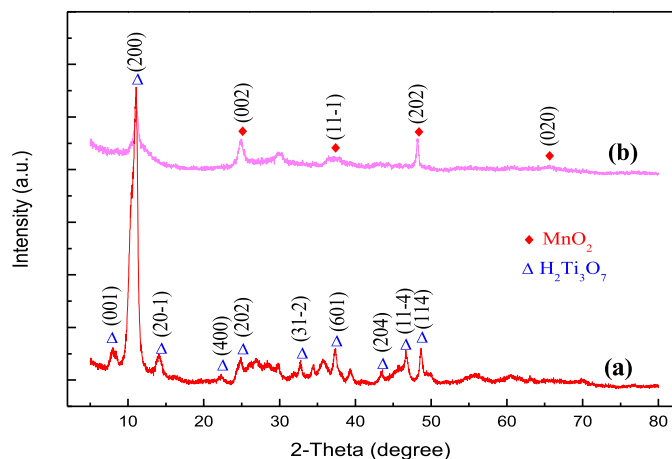
Fig. 1. XRD patterns of pure $H_2Ti_3O_7$ NWs (a) and $MnO_2/H_2Ti_3O_7$ NWs (b).

indexed to $H_2Ti_3O_7$ (JCPDS NO. 41-0192) and monoclinic potassium birnessite MnO_2 (JCPDS NO. 86-0666). The sharp and strong peaks for as-prepared $H_2Ti_3O_7$ attest the good crystallinity and high purity. After MnO_2 decoration (Fig. 1b), the diffraction peak from the birnessite-type MnO_2 phase is weak, indicating a low mass loading of MnO_2.

TEM images (Fig. 2a) exhibit that MnO_2 nanosheets-coated $H_2Ti_3O_7$ NWs have uniform diameter (about 80 nm), slightly larger than pristine $H_2Ti_3O_7$ NWs (ca. 60 nm; see Supplementary information, SI-1). These as-formed MnO_2 nanosheets with a diameter of 5−10 nm are intercrossed with each other, which create loose porous nanostructures with abundant open space and electroactive surface sites (Fig. 2b). Interestingly, increasing the reaction time to 30 h, the MnO_2 nanoflakes grow larger and the diameters increase to ~20 nm (SI-2). A high-resolution TEM image (Fig. 2c and d) taken from the zones of the $MnO_2/H_2Ti_3O_7$ NWs (indicated in Fig. 2b) illustrates that the well-resolved lattice fringe gives an interplanar spacing of 0.36 nm, which is well consistent with the distance of the (110) plane of $H_2Ti_3O_7$ (Fig. 2d). Meanwhile, the interplanar spacing of MnO_2 nanoflake is 0.71 nm (Fig. 2c), which is the typical interplanar spacing of birnessite-type MnO_2 as reported in other literature [35,36]. The selected area electron diffraction (SAED) pattern demonstrates that the $H_2Ti_3O_7$ NWs are monocrystalline (inset in Fig. 2c). The inset in Fig. 2d presents the SAED pattern of the hybrid, and the two diffraction rings are corresponding to the (002) and (113) crystal planes of MnO_2.

Fig. 3 shows the XRD pattern of TiO_2 NWs and MnO_2/TiO_2 NWs. Diffractions from the anatase phase (JPCDS 21-1272) and TiO_2 (B) phase (JPCDS 35-0088) are observed after calcination at 400 °C (Fig. 3a), indicating that these nanowires are of mixed anatase and TiO_2(B) phase. The peaks associated with TiO_2 (B) are more prominent than that of anatase, indicative of better crystallinity of TiO_2 (B). As for the MnO_2/TiO_2 NWs (Fig. 3b), diffraction peaks from the birnessite-type MnO_2 phase can be observed and the diffraction intensity of the peaks from the TiO_2 phase decreases evidently, indicating a high mass loading of MnO_2.

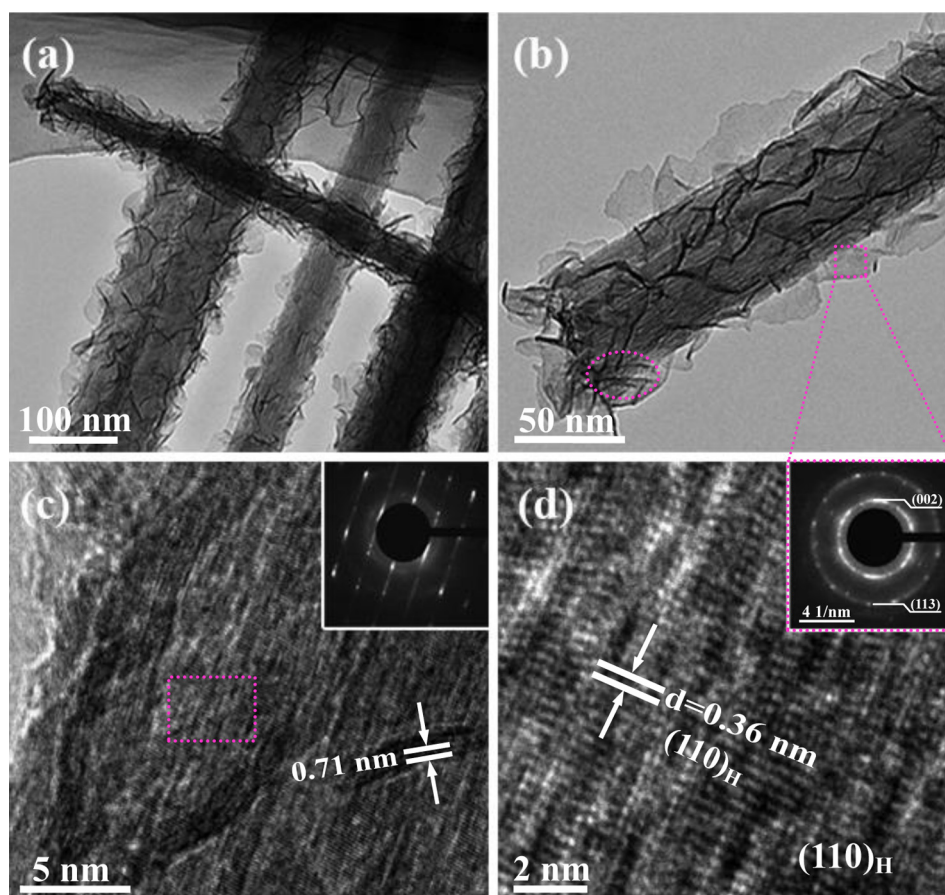**Fig. 2.** (a) Low- and (b) high-magnification TEM images of the $MnO_2/H_2Ti_3O_7$ NWs, (c, d) HRTEM images of the $MnO_2/H_2Ti_3O_7$ NWs. The insert of (c) and (d) are the SAED patterns from the $MnO_2/H_2Ti_3O_7$ NWs and MnO_2 nanoflakes respectively.
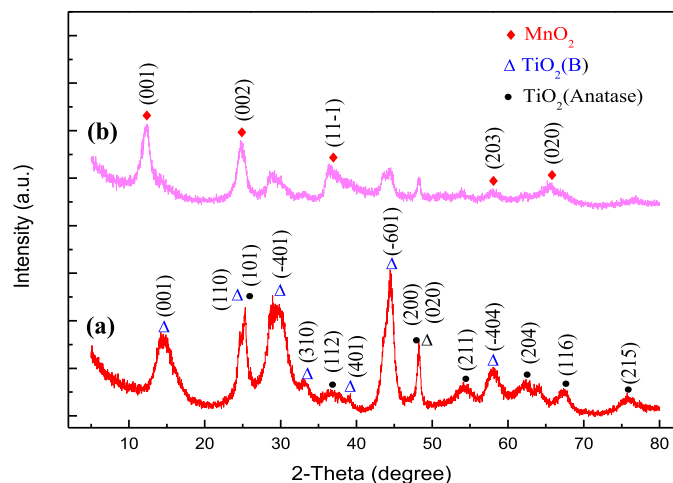
Fig. 3. XRD patterns of anatase/TiO$_2$ (B) NWs (a) and MnO$_2$/TiO$_2$ NWs (b).

The low-magnification SEM and TEM images (SI-1) clearly show an individual TiO$_2$ NWs with diameter of about 80 nm and lengths of several hundred nanometers. Apparently, after oxidative conversion into mixed phase anatase-TiO$_2$ (B), the basic morphology of the sample is perfectly conserved without calcination-induced significant alterations. After MnO$_2$ decoration, the surface of TiO$_2$ is homogeneously covered with a layer of dense MnO$_2$ ultrathin nanoflakes (Fig. 4a). The interconnected MnO$_2$ nanosheets create a highly porous surface morphology. This configuration can provide

an especially high surface area and more active sites for the adsorption of Na$^+$, which hence endows the MnO$_2$ with a very high specific capacitance.

The energy-dispersive X-ray spectroscopy (EDX) (see Supplementary information, SI-3) shows clear evidence of core/shell linear structure with the Mn signal peaks at the outside (shell) of the composite and the Ti signal peak at the inner part (core) of the wire. The interface between MnO$_2$ and TiO$_2$ can be distinguished from the gray scale contrast across the nanowire (Fig. 4b), and the nanoflake with diameters of about 30 nm can be clearly observed. Higher-magnification TEM images (Fig. 2c and d) reveal that the interplanar spacing of MnO$_2$ nanoflake is 0.71 nm, indicative of birnessite-type MnO$_2$ nanoflakes. The SAED pattern (inset of Fig. 4c) reveals the single-crystalline nature of TiO$_2$ NWs and the polycrystalline nature of MnO$_2$. The HRTEM image (Fig. 2d) reveals two sets of lattice fringes with interplane spacings of 0.32 and 0.27 nm, corresponding to the (002) and (310) planes of anatase and TiO$_2$ (B) phase, respectively.

The nitrogen adsorption and desorption isotherms of the MnO$_2$/H$_2$Ti$_3$O$_7$ and MnO$_2$/TiO$_2$ NWs are shown in Fig. 5. The N$_2$ adsorption–desorption isotherm is characteristic of type IV with a type H3 hysteresis loop observed in the range 0.7–1.0 P/P_0 (Fig. 5a and b) [3], which suggests the presence of a mesoporous structure for the MnO$_2$/H$_2$Ti$_3$O$_7$ and MnO$_2$/TiO$_2$ NWs [37,38]. The Brunauer–Emmett–Teller (BET) surface area value of the MnO$_2$/H$_2$Ti$_3$O$_7$ and MnO$_2$/TiO$_2$ NWs is calculated to be 39.8 and 57.8 m^2 g^{-1}, respectively, which is higher than the pristine H$_2$Ti$_3$O$_7$ and TiO$_2$ NWs (see Supplementary information, SI-4). The pore size distribution of the sample calculated by desorption isotherm using
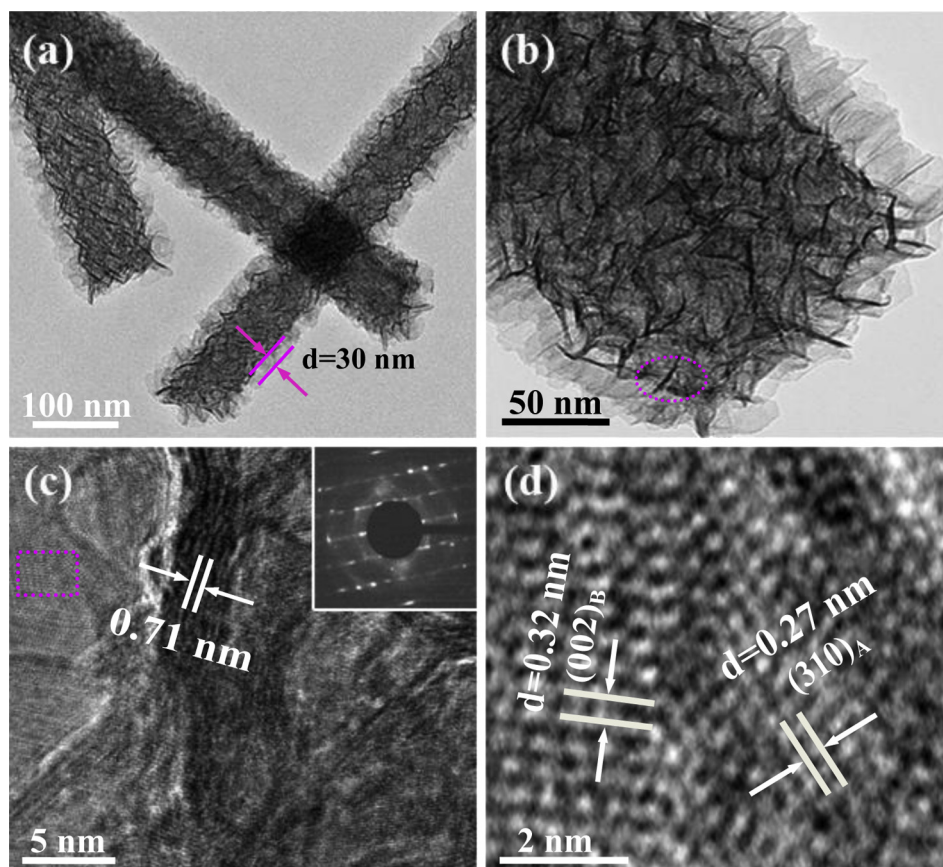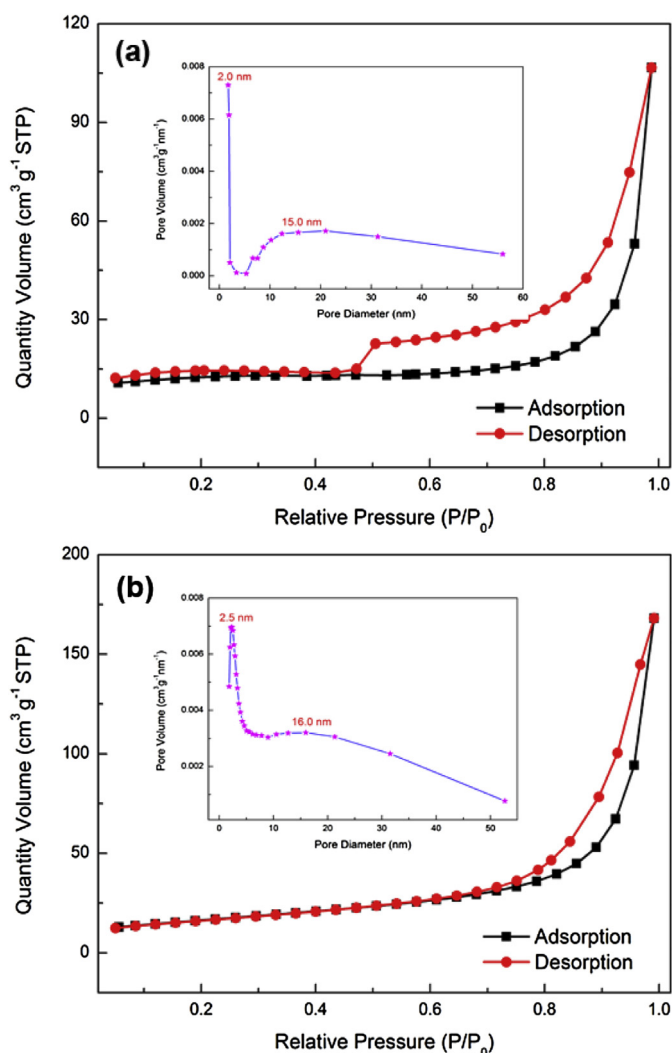

Fig. 4. (a) Low- and (b) high-magnification TEM images of the MnO$_2$/TiO$_2$ NWs; (c, d) HRTEM images of the MnO$_2$/TiO$_2$ NWs. The insert of (c) is the SAED patterns from the region marked with a rectangle in (b).

Fig. 5. Nitrogen adsorption and desorption isotherms for the $MnO_2/H_2Ti_3O_7$ NWs (a), and MnO_2/TiO_2 NWs (b). The insets show the corresponding BJH pore size distributions.

calculated as 0.158 $cm^3\ g^{-1}$, while the pore volume of MnO_2/TiO_2 NWs is up to 0.261 $cm^3\ g^{-1}$. Inconsideration of high surface area and large pore volume, it is expected that the MnO_2/TiO_2 NWs will have impressive electrochemical performance, and further electrochemical measurements have been carried out to prove this hypothesis.

On the basis of observations above, the mass loading of MnO_2 nanoflakes in $H_2Ti_3O_7$ and TiO_2 NWs is very different, as illustrated in Fig. 6a. $H_2Ti_3O_7$ is annealed in air at 400 °C for 2 h; the surface of TiO_2 NWs becomes highly porous and active. In addition, FTIR spectra are examined to uncover the surface characteristics of nanowires (Fig. 6b). The basic crystal structure units of $H_2Ti_3O_7$ NWs are $[Ti_3O_7]^{2-}$ sheets, which will stop $[MnO_4]^-$ approaching nanowires due to electrostatic repulsion, while the abundant hydroxyl of TiO_2 NWs speed up the oxidation. It is assumed that surface properties of diverse nanowires would also lead to different deposition density of MnO_2 nanosheets as well as the calcinations and processing time. Additionally, the chemical composition of MnO_2/TiO_2 and $MnO_2/H_2Ti_3O_7$ are calculated by etching the MnO_2 in HCl solution (37 wt.%) (see Supplementary information, Table S1). The MnO_2/TiO_2 mass ratio is 36/64 while the $MnO_2/H_2Ti_3O_7$ mass ratio is 22/78. It is apparent that MnO_2/TiO_2 NWs has higher mass ratio of MnO_2 compared with $MnO_2/H_2Ti_3O_7$ NWs under similar feed mass ratio of Ti-based NWs/$KMnO_4$ and reaction condition, suggesting that the surface of TiO_2 NWs contributes to the growth of MnO_2 nanosheets.

Herein, a general growth mechanism for the unique MnO_2/TiO_2 NWs is proposed, on the basis of above analysis and SI-5. When the mixed solution of TiO_2 and $KMnO_4$ solution is treated under hydrothermal condition for 4 h, the TiO_2 NWs surfaces become rough, initially decorated by many tiny MnO_2 "buds" which are produced by the decomposition of $KMnO_4$. With the reaction time increases to 8 h, the rudiments of MnO_2 nanosheets are formed, and then fully develop when the reaction time is prolonged to 24 h. Moreover, increasing the reaction time to 30 h, the MnO_2 nanosheets grow larger and the morphologies of bending, curling, and crumpling are clearly observed (SI-5 and SI-6).

3.2. Electrochemical performances

The transportation of electrolytes through the MnO_2/TiO_2-based nanostructures is feasible for efficient redox reactions during Faradaic charge storage process because of their hierarchical structure. However, the charge storage efficiency of these structures may vary because of their observed differences (e.g., the morphology and size). To evaluate their electrochemical

Barret–Joyner–Helenda (BJH) method is shown in inset of Fig. 5. The $MnO_2/H_2Ti_3O_7$ NWs show a narrow pore size distribution centered at around 1.5 nm, while the MnO_2/TiO_2 NWs have sharp peak at ~2.5 nm. The pore volume of $MnO_2/H_2Ti_3O_7$ NWs is

Fig. 6. (a) Schematic diagram illustrating the processes for growth MnO_2 nanoflakes on $H_2Ti_3O_7$ and anasate/TiO_2 (B) NWs; (b) FTIR of pristine $H_2Ti_3O_7$ and TiO_2 NWs.

performance, cyclic voltammetry (CV) and galvanostatic charge–discharge measurements are performed. Representative CV curves for the MnO_2/TiO_2 and $MnO_2/H_2Ti_3O_7$ NWs in three electrode configuration at different scan rates are shown in Fig. 7a and b. Both $MnO_2/H_2Ti_3O_7$ and MnO_2/TiO_2 NWs exhibit ideal rectangular and symmetric CV curves at low scanning rates (5 and 10 mV s^{-1}), proving the ideal pseudo-capacitive nature with fast charge–discharge process [39]. Furthermore, the CV profile of $MnO_2/H_2Ti_3O_7$ NWs deviates seriously from rectangularity and transforms into spindle shape with increasing scanning rates, especially at a high scan rate of 50 mV s^{-1}. This can be ascribed to poor electrical conductivity of $MnO_2/H_2Ti_3O_7$ NWs and the change of ion transplant surrounding, for which the ions can only reach the

outer surface of the electrode and cannot enter into the interior pores at a large scan rate [17,40]. In contrast, MnO_2/TiO_2 NWs present close-rectangular CV curves over in wide range of scanning rates (5–50 mV s^{-1}). This is because MnO_2/TiO_2 NWs nanostructures have relatively appropriate pore size and surface texture. Furthermore, the existence of TiO_2 facilitates charge transfer to the MnO_2 phase. The area of MnO_2/TiO_2 NWs under the CV curve is clearly much larger than that of $MnO_2/H_2Ti_3O_7$ NWs at the same scan rate, suggesting a high specific capacitance and utilization of MnO_2 in the hybrids.

The galvanostatic charge/discharge (GCD) tests of the MnO_2/TiO_2 and $MnO_2/H_2Ti_3O_7$ NWs at different constant current densities (Fig. 6c and d) present that the curve of MnO_2/TiO_2 NWs is linear and
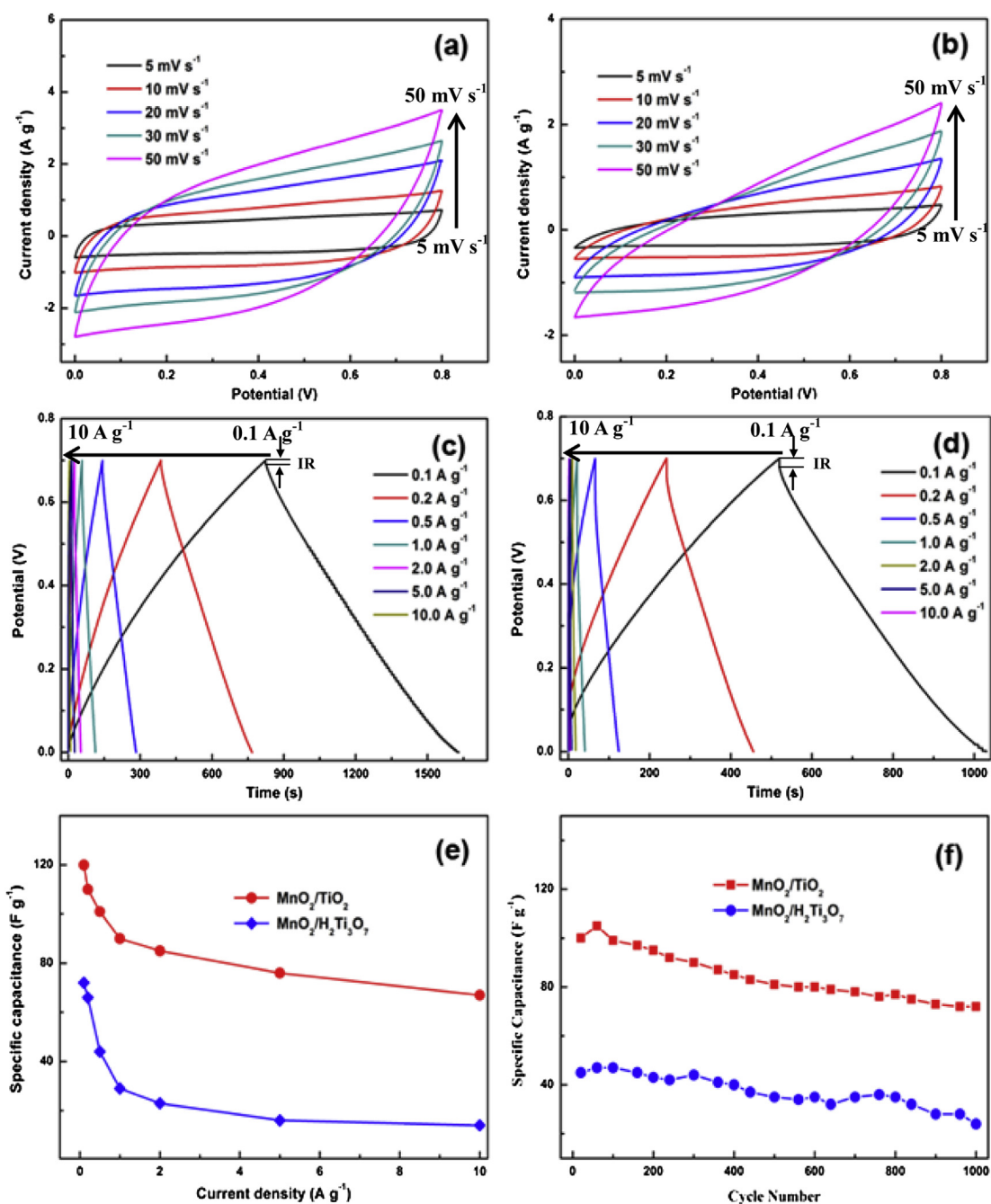

Fig. 7. (a, b) CV curves, (c, d) charge–discharge curves, (e) capacitances versus current densities, and (f) variation of capacitance with cycle number at 0.3 A g^{-1} of the (a, b) MnO_2/TiO_2 NWs and the (c, d) $MnO_2/H_2Ti_3O_7$ NWs.

symmetric, indicating an ideal capacitor, capable of reversible charging and discharging [41]. In comparison, the curve of MnO_2/$H_2Ti_3O_7$ NWs is distorted to some extent. Furthermore, the IR drop (marked in Fig. 6c and d) of MnO_2/TiO_2 NWs is much lower than that of MnO_2/$H_2Ti_3O_7$ NWs, indicating that the introduction of TiO_2 reduces significantly internal resistance. Low internal resistance is very favorable in energy storage devices, which reduces energy waste during charging/discharging processes. The increase in the charging time represents the higher capacitance of the MnO_2/TiO_2 NWs. According to the GCD curves, the specific capacitances of the electrodes are respectively calculated using the following equation [42]:

$$C_m = \frac{I\Delta t}{m\Delta V}$$

where m, I, Δt and ΔV are the weight (g) of the electroactive materials, discharge current (A), the discharging time (s), and the discharging potential range (V), respectively. The specific capacitance of MnO_2/TiO_2 and MnO_2/$H_2Ti_3O_7$ NWs obtained from the discharging curves are calculated to be 120 F g^{-1} and 72 F g^{-1} at the current density of 0.1 A g^{-1}, respectively. It is due to that the highly porous structure and high specific surface area of the TiO_2 shell facilitate the ions to transfer into the porous structure more easily which would lead to substantial redox faradic reactions and surface adsorption of electrolyte cations. Maximizing the utilization of MnO_2 is always considered as a challenge because only the surface of oxides can be utilized for charge storage. Herein, the comparison of the specific capacitance (based on the mass of MnO_2 alone) between this work and previous reports is summarized (Table S2). The normalized specific capacitance of MnO_2/TiO_2 NWs in this work is 334 F g^{-1} at the current density of 0.1 A g^{-1}, much higher than that of MnO_2/activated carbon electrode (228 F g^{-1}) [43], MnO_2–graphene composites electrode (234.2 F g^{-1}) [44], RGO/MnO_2 electrode (260 F g^{-1}) [45], and graphene/MnO_2/polyaniline electrode (276 F g^{-1}) [36].

The rate capability of MnO_2/TiO_2 and MnO_2/$H_2Ti_3O_7$ NWs is also evaluated by charging–discharging at different current densities (Fig. 7e). The MnO_2/TiO_2 NWs maintain their 58.9% capacitance as the current density is increased from 0.1 to 10 A g^{-1}, while the MnO_2/$H_2Ti_3O_7$ NWs lose 80.6% of their capacity in the same condition, indicating that the MnO_2/TiO_2 NWs have better rate capability, in good accordance with the CV tests. Additionally, the specific capacitance based on MnO_2 mass alone versus current density is addressed in Table S3.

The cycling stability of MnO_2/TiO_2 and MnO_2/$H_2Ti_3O_7$ NWs in 1 M Na_2SO_4 electrolyte at a current density of 1 A g^{-1} is shown in Fig. 7f. The specific capacitance of MnO_2/TiO_2 NWs increases in the initial 60 cycles owing to the improved wetting by applying a potential, and then only a little fading can be observed and the capacitance retention is 95% after 1000 cycles. As for the MnO_2/$H_2Ti_3O_7$ NWs the decay in specific capacitance after a 1000-cycle test is 40%. These results also indicate that the MnO_2/TiO_2 NWs have a better cycling performance, in comparison with the MnO_2/$H_2Ti_3O_7$ NWs.

The EIS analysis has been recognized as one of the principal methods for examining the fundamental behavior of electrode materials, which not only provides useful information on the electrochemical frequency of the system but also allows for the measurement of redox reaction resistance and equivalent series resistance of the electrode [40]. As presented in Fig. 8, the Nyquist plots can be divided into two parts:one semicircle in the high-frequency, and a straight line inclining about 45° to the real axis or an almost vertical line in the low frequency region [46–48]. At the high frequencies, semicircles can be observed with the diameters representing the charge-transfer resistance (R_{ct}) [46]. It is apparent that MnO_2/TiO_2 NWs have a much smaller R_{ct} than MnO_2/
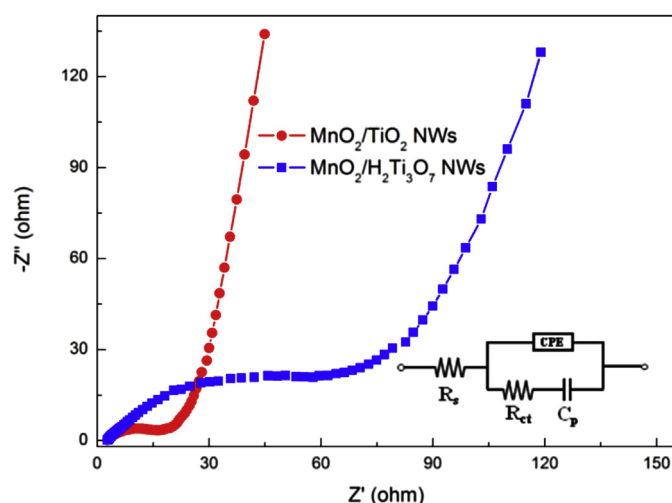

Fig. 8. Nyquist plots for MnO_2/TiO_2 and MnO_2/$H_2Ti_3O_7$ NWs in the frequency range of 100 kHz–0.01 Hz. Insert shows the equivalent circuit for the electrochemical impedance spectrum.
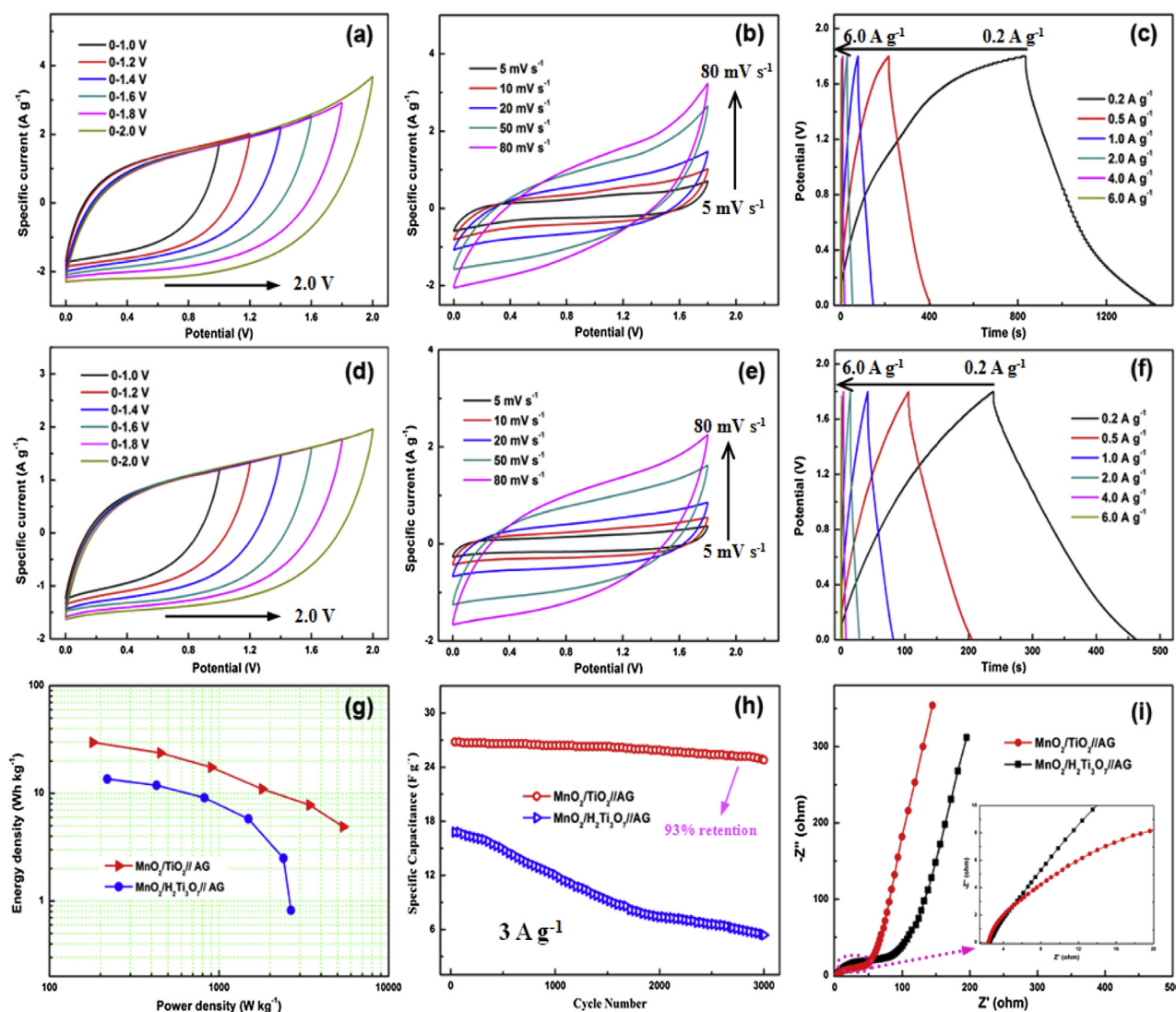
$H_2Ti_3O_7$ NWs. The slope of 45° portion in the transitory frequency next to the semicircle and the noticeable linear part at the low frequency region of the respective Nyquist plots is called Warburg resistance (W) [49], which originates from the frequency dependence of ion diffusion/transport from the electrolyte to the electrode surface [50,51]. As shown in the Fig. 8, MnO_2/TiO_2 NWs electrode has a smaller Warburg region, presenting a minor Warburg resistance. It implies that the highly porous MnO_2/TiO_2 NWs are able to facilitate the penetration of electrolyte, leading to fast diffusion of electrolyte into the pores of MnO_2. It can be seen that the slope of the straight line for the MnO_2/TiO_2 NWs is much larger than that of the MnO_2/$H_2Ti_3O_7$ NWs. This observation indicates that the MnO_2/TiO_2 NWs have much lower diffusive resistance than the MnO_2/$H_2Ti_3O_7$ NWs. After cycling for 1000 times (SI-7), the R_s of MnO_2/TiO_2 and MnO_2/$H_2Ti_3O_7$ NWs increase from 1.5 and 1.8 Ω to 2.6 and 2.9 Ω, respectively. EIS analytical results further verify that MnO_2/TiO_2 NWs exhibits good cycling stability compared with MnO_2/$H_2Ti_3O_7$ NWs, which is attributed to the following factors: (1) the conductive electronic and ion transport capability of unique architecture of anatase/TiO_2 (B) mixed-phase system is higher than that of $H_2Ti_3O_7$ NWs, which is due to the heterojunction of anatase/TiO_2(B) mixed-phase. (2) The pristine anatase/TiO_2(B) NWs have larger surface area, pore volume and higher pore size distribution compared with pristine $H_2Ti_3O_7$ NWs (SI-4), which endow the MnO_2/TiO_2 NWs with more electron/ion paths for feasible ion transport and fast redox reaction.

The as-prepared MnO_2/TiO_2, MnO_2/$H_2Ti_3O_7$ NWs and AG materials can be used as freestanding electrodes for assembling asymmetric and symmetric supercapacitor cells. CV and GCD measurements were firstly performed to evaluate the electrochemical potential windows and quantify the specific capacitances of these electrodes in a 1 M Na_2SO_4 aqueous electrolyte using a three electrode system. The AG was measured within a potential window of −1 to 0 V. The relatively rectangular shape of CV curve (see Supplementary information, SI-8a) is mirror-symmetric with good reversibility, indicating excellent double-layer capacitive behavior for AG electrode. Additionally, the AG electrode exhibits a specific capacitance of 106 F g^{-1} at the current density of 0.5 A g^{-1} in the potential range of −1 to 0 V (see Supplementary information, SI-8b). Therefore, the optimal positive/negative mass ration of MnO_2/TiO_2 and AG was set almost 1.50 and MnO_2/$H_2Ti_3O_7$ and AG was set almost 3.44 based on the balance of the charges (Q).

Based on the above electrochemical characteristics investigation of the individual capacitor, it is possible to combine MnO_2/TiO_2 or $MnO_2/H_2Ti_3O_7$ NWs (positive electrode) and AG (negative electrode) to obtain an asymmetric capacitor with a potential window close to 1.8 V. Fig. 9a and b exhibits CV curves of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor cell at different potential windows in 1 M Na_2SO_4 aqueous solution at 60 mV s^{-1}. The fabricated asymmetric supercapacitor presents an ideal capacitive behavior with rectangular CV curve. At a potential window of 2.0 V, the CV curve shows a distortion and a slight hump around 2.0 V. This indicates that some irreversible reactions happen when the potential window is higher than 1.8 V [52]. Thus, the optimum working potential window for this asymmetric supercapacitor is from 0 to 1.8 V. Fig. 9b, e exhibits the variation of the specific capacitance with the increase of potential window for the asymmetric supercapacitor. The CV profile of the asymmetric cell remains relatively rectangular at a high scan rate of 80 mV s^{-1}, demonstrating good charge/discharge properties and rate capability of the asymmetric supercapacitor [33]. As shown in Fig. 9c, f the potential of the charge–discharge lines are

nearly proportional to the charge or discharge time, a small equivalent series resistance and an ideal capacitive characteristic, as further confirmed by the EIS date (Fig. 9i). The gravimetric capacitance of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor are calculated to be 66.1 and 32 F g^{-1} based on the total weight of the electrodes, respectively.

To further illustrate the energy and power property of this asymmetric supercapacitor, a Ragone plot is shown in Fig. 9g. In comparison to the $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor, the energy densities of the $MnO_2/TiO_2//AG$ asymmetric supercapacitor are dramatically higher, especially in cases with lower power densities. A maximum energy density of $MnO_2/TiO_2//AG$ asymmetric supercapacitor29.8 Wh kg^{-1} is obtained for the $MnO_2/TiO_2//AG$ asymmetric supercapacitor, which is more than twice that of the $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor (13.6 Wh kg^{-1}). This result shows an improved energy density compared with a $MnO_2/SiO_2//MnO_2/SiO_2$ symmetric device (3.75 Wh kg^{-1}) [53], a CNT/MnO_2/GR//CNT/PANI asymmetric device (24.8 Wh kg^{-1}) [6], and a MnO_2/carbon nanofiber//active

Fig. 9. (a, d) CV curves of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor cell measured at different potential windows in 1 M Na_2SO_4 electrolyte, respectively; (b, e) CV curves of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor cell measured at different scan rates, respectively; (c, f) charge–discharge curves of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor, respectively; (g) Ragone plot of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor at the frequencies ranging from 100 kHz to 0.1 Hz. The inset shows the enlarged high frequency range; (h) cycling performance of $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor for charging and discharging at a current density of 3 A g^{-1}; (i) Nyquist plot of the $MnO_2/TiO_2//AG$ and $MnO_2/H_2Ti_3O_7//AG$ asymmetric supercapacitor.

carbon nanofiber asymmetric device (8.2 Wh kg^{-1}) [25]. In addition, the specific capacitance, power density, and energy density of the asymmetric supercapacitor at different current densities are also listed in Table S4.

Long cycling life is an important requirement for supercapacitors. The cycling life test over 3000 cycles for the MnO$_2$/ TiO$_2$//AG and MnO$_2$/H$_2$Ti$_3$O$_7$//AG asymmetric supercapacitor is carried out by repeating the GCD test between 0 and 1.8 V at a current density of 3 A g^{-1} for 3000 cycles (Fig. 9h). The specific capacitance of MnO$_2$/H$_2$Ti$_3$O$_7$//AG asymmetric supercapacitor decreases gradually with increasing cycle numbers and its capacitance retention is only 33% after 3000 cycles. By contrast, MnO$_2$/ TiO$_2$//AG asymmetric supercapacitor only a little fading can be observed and the capacitance retention is 93%after 3000 cycles.

As previously shown, the MnO$_2$/TiO$_2$//AG asymmetric supercapacitor introduces the advantages of the synergism between the two metal-oxides nanomaterials, and these results highlight the capability of the MnO$_2$/TiO$_2$//AG asymmetric supercapacitor to meet the requirements of both high specific capacitance and excellent stability, which are important merits for practical energy storage devices.

4. Conclusion

In conclusion, we have prepared ultrathin MnO$_2$ nanoflakes on H$_2$Ti$_3$O$_7$ and TiO$_2$ NWs via a facile hydrothermal route. Each H$_2$Ti$_3$O$_7$ or TiO$_2$ NWs renders direct contact with the MnO$_2$ and creates unique supercapacitor electrodes. In view of the difference of surface area and pore volume, the two nanostructures present different pseudocapacitive performance. Electrochemical measurements reveal that the MnO$_2$/TiO$_2$ NWs exhibits much higher specific capacitance and better rate capability compared with MnO$_2$/H$_2$Ti$_3$O$_7$ NWs. This is because the TiO$_2$ NWs not only provide high surface area for the deposition of MnO$_2$ nanoflakes but also improve the electrical conductivity. Therefore, the rational design of MnO$_2$/TiO$_2$ NWs can be used for large-scale fabrication of other promising supercapacitors as well as other power source systems.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.07.114.

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